

oxidizing products just before use, these intermediary substances can produce colored compounds or colorants through a process of oxidative condensation. This is the reason why the term of "oxidation dyes" was retained.

In general, they are aromatic compounds belonging to three major chemical families: the diamines, aminophenols (or amino naphthols) and the phenols (or naphthols).

The oxidation dyes most currently used are in the following classes:

A. Aromatic Diamines

- B₁* 1,4-diamino-benzene (*p*-phenylenediamine)
- B₂* 2-methyl-1,4-diamino-benzene (*p*-tolylenediamine)
- B₃* 2-chloro-1,4-diamino-benzene (*o*-chloro-*p*-phenylenediamine)
- B₆* 4-amino diphenylamine (N-phenyl *p*-phenylenediamine)
- B₈* 1-amino-4- β -methoxyethylamino-benzene (N- β -methoxyethyl-*p*-phenylenediamine)
- B₉* 1-amino-4-bis-(β -hydroxyethyl)-aminobenzene (N,N-bis-(β -hydroxyethyl)-*p*-phenylenediamine)
- C₁* 1,3-diamino-benzene (*m*-phenylenediamine)
- C₃* 2-methyl-1,3-diamino-benzene (2,6-diaminotoluene)
- C₄* 2,6-diaminopyridine

B. Aminophenols

- B₇* 1-hydroxy-2-amino-benzene (*o*-aminophenol)
- C₅* 1-hydroxy-3-amino-benzene (*m*-aminophenol)
- C₁₅* 1-methyl-2-hydroxy-4-amino-benzene (3-amino *o*-cresol)
- C₁₃* 1-methyl-2-hydroxy-4- β -hydroxyethylamino-benzene (2-hydroxy-4- β -hydroxyethylamino-toluene)
- B₄* 1-hydroxy-4-amino-benzene (*p*-aminophenol)
- B₅* 1-hydroxy-4-methylamino-benzene (*p*-methylaminophenol)
- C₂* 1-methoxy-2,4-diamino-benzene (2,4-diaminoanisole)
- C₁₆* 1-ethoxy-2,3-diamino-benzene (2,4-diaminophenetol)
- C₁₂* 1- β -hydroxyethoxy-2,4-diamino-benzene (2,4-diaminophenoxyethanol)

C. Phenols (or Naphthols)

- C₈* 1,2-dihydroxybenzene (pyrocatechol)
- C₉* 1,3-dihydroxybenzene (resorcinol)
- C₁₄* 1,3-dihydroxy-2-methylbenzene (2-methyl resorcinol)
- 1,3-dihydroxy-4-chlorobenzene (4-chloro resorcinol)

C_{11} 1,2,3-trihydroxybenzene (pyrogallol)
 1,2,4-trihydroxybenzene
 1,2,4-trihydroxy-5-methylbenzene (2,4,5-trihydroxytoluene)
 C_{10} 1,5-dihydroxynaphthalene
 C_7 1,4-dihydroxybenzene (hydroquinone)
 C_6 1-hydroxynaphthalene (α -naphthol)

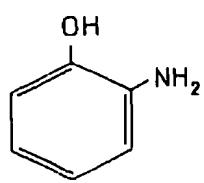
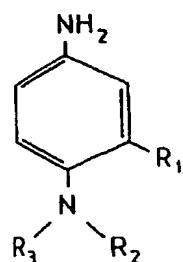
On white hair, deep shades can only be obtained using the aromatic amines, or the aminophenols with amino and hydroxyl groups in *ortho* or *para* position to each other. Thus, only compounds capable of producing the quinone monoimine or quinone diimine forms yield highly colored pigments through oxidation. Similarly, it has been observed that copolymerization does not result in deep shades unless quinone monoimines or quinone diimines participate in the condensation. One of the intermediaries in the copolymerization must almost always be an *ortho*- or *para*-diamine or aminophenol. This observation leads to a classification of oxidation products that is not one of simple differentiation by chemical class.

The so-called *bases* or primary intermediates are the aromatic diamines, the diaminophenols, the aminophenols with amino or hydroxy groups *para* or *ortho* to each other.

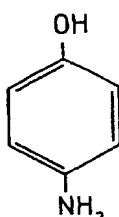
The "modifiers" or *couplers* are the *m*-diamines, the *m*-aminophenols, and the polyphenols. Taken separately, all these modifiers yield only feeble coloring through oxidation; cooxidation of modifier mixes, too, yield only slight coloring (yellow, blond-beige).

Table 1

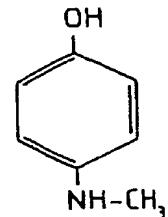
Base	R ₁	R ₂	R ₃
B ₁	H	H	H
B ₂	CH ₃	H	H
B ₃	Cl	H	H
B ₆	H	C ₆ H ₅	H
B ₈	H	CH ₂ -CH ₂ -OCH ₃	H
B ₉	H	CH ₂ -CH ₂ OH	CH ₂ -CH ₂ OH



B₇



B₄



B₅

A simple classification of the major oxidation dyes, taking these facts into account, would be as follows:

Bases (Table 1):

- B*₁ *p*-phenylenediamine (PPD)
- B*₂ *p*-toluylenediamine (PTD)
- B*₃ chloro-*p*-phenylenediamine
- B*₆ N-phenyl-*p*-phenylenediamine
- B*₈ N- β -methoxyethyl-*p*-phenylenediamine
- B*₉ N,N-bis-(β -hydroxyethyl)-*p*-phenylenediamine
- B*₇ *o*-aminophenol
- B*₄ *p*-aminophenol
- B*₅ N-methyl-*p*-aminophenol

Couplers (Table 2):

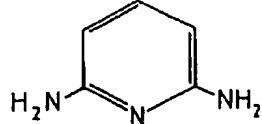
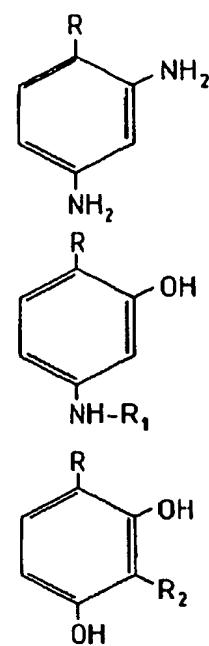
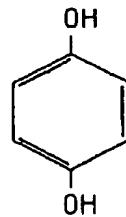
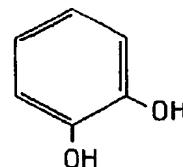
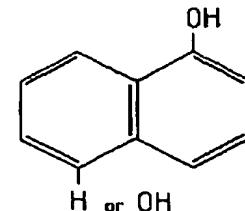
- C*₁ *m*-phenylenediamine
- C*₃ 2,4-diaminotoluene
- C*₅ *m*-aminophenol
- C*₁₅ 3-amino-*o*-cresol
- C*₁₃ N- β -hydroxyethyl-*m*-aminocresol (2-hydroxy-4- β -hydroxyethylamino-toluene)
- C*₂ 2,4-diaminoanisole
- C*₁₆ 2,4-diaminophenetole
- C*₁₂ 2,4-diaminophenoxyethanol
- C*₈ pyrocatechol
- C*₉ resorcinol
- C*₁₄ 2-methylresorcinol
- C*₄ 2,6-diaminopyridine
- C*₁₇ 4-chlororesorcinol
- C*₁₁ Pyrogallol
 - 1,2,4-trihydroxybenzene
 - 1,2,4-trihydroxytoluene
- C*₁₀ 1,5-dihydroxynaphthalene
- C*₇ hydroquinone
- C*₆ α -naphthol

In addition to these considerations on the relative positions of the auxochrome groups, one can attempt to define the influence on the nature and intensity of color of certain substitutions in the benzene ring or in the auxochrome groups themselves.

- I. The introduction of nitro groups in the benzene ring yields yellow, red, or purple-violet shades.

Table 2

Coupler	R	R ₁	R ₂
C ₁	H		
C ₃	CH ₃		
C ₂	OCH ₃		
C ₁₆	OCH ₂ -CH ₃		
C ₁₂	OCH ₂ -CH ₂ OH		
C ₅	H	H	
C ₁₅	CH ₃	H	
C ₁₃	CH ₃	CH ₂ -CH ₂ OH	
C ₉	H		H
C ₁₆	H		CH ₃
C ₁₇	Cl		H
C ₁₁	H		OH

C₄C₇C₈C₆ or C₁₀

- Increasing the number of amino groups facilitates and accelerates the dyeing process. However, this does not necessarily mean a deepening in color. The triamine compounds produce a red or brown color, whereas the corresponding diamines yield black or dark brown.
- Increasing the number of hydroxy groups in relation to the amino groups diminishes the intensity of the shade.
- Only the polyhydroxylated compounds with OH groups *ortho* or *para* to each other possess useful dyeing properties. *m*-Diphenol (resorcinol) only colors very slightly. But all of these can participate in copolymerization through oxidation.
- Substituting methoxy or ethoxy groups for hydroxyl groups weakens color but renders shades more durable.
- Methyl or ethyl group in the benzene ring results in a reduction of dyeing power.
- A chlorine atom *para* to the NH₂ or OH group will deepen the shade, but if it is *ortho* or *meta*, the shade will be attenuated.

Very often, and in particular to obtain shades with reddish highlights (coppery, purple-violet, dark auburn), "direct" dyes are added to the oxidation dyes. They belong sometimes to the azoic or triphenylmethane classes, in so far as they sufficiently stand light. More generally, aromatic nitro derivatives are used, which although belonging either to the amine or diamine class or the phenol or aminophenol class, cannot be considered as oxidation dyes. They do not participate either in the oxidation itself or in the oxidative condensations. Their unique role as an additive is to provide the highlight.

II. THE OXIDATION MECHANISMS

This is a complicated process. Each of the precursors defined above (*base* or *coupler*) can, through oxidation and polymerization, produce a pigment that will fix on keratin.

It is common knowledge that oxidation of *p*-phenylenediamine yields the corresponding quinone diimine, and that oxidation of *p*-aminophenol generates quinone monoimine. If the oxidation occurs in the presence of phenols or *m*-aminophenols, which may be substituted on the ring by halogen atoms or CH_3 , or OCH_3 radicals, for instance, and providing the *para* position to the phenol remains free, the quinone diimine condense on these compounds, resulting in the formation of indoanilines, while from the quinone monoimine, there is formation of indophenols.

The series of chemical reactions can be described without too much difficulty in the case of the oxidation of a *base* on its own or of binary *base-coupler* mixes. It is much harder to describe the mechanism of oxidative copolymerization once there are three, four, or five precursors present, which is a common occurrence in hair dye formulation.

By way of an example, one may describe the condensation of *p*-phenylenediamine (PPD) on itself and the couplings of *p*-phenylenediamine with *m*-phenylenediamine and resorcinol, respectively.

